

APPLE SIRUP by ION EXCHANGE PROCESS

R. E. Buck and H. H. Mottern

EASTERN REGIONAL RESEARCH LABORATORY
U. S. DEPARTMENT OF AGRICULTURE
PHILADELPHIA 18, PA.

MANY attempts have been made to produce an apple sirup of satisfactory flavor for food uses. An apple sirup developed in this laboratory has found industrial application as a moisture-retaining agent because of its high levulose content (1, 7). It is objectionable for food uses, however, because of a slightly bitter aftertaste due to the calcium malate formed in the liming process.

The ability of ion exchangers to remove acid and basic constituents from solution suggested their possible use in preparing an edible sirup. Removal of malic acid prior to liming would prevent the formation of calcium malate. It was thought that ion exchanger treatment might also reduce the lead and arsenic contents.

A number of applications of ion exchangers to process industries have been reported. Englis and Fiess (8) state that elimination of the acid and mineral constituents from artichoke extract by ion exchangers produced a sirup of improved quality and flavor. They found that the ash content was reduced to about two thirds of its original value by one cation exchanger treatment and to one fourth by two treatments. Aside from the effect on the pH value of the extract, no data were reported on the actual amount of acid constituents removed by the anion exchanger. Ion exchangers removed 87% of nonsugar solids from beet and sugar cane juices (11, 14); they were slightly more effective in removing inorganic than organic impurities. The treatment also resulted in an increased purity and higher yields of sugar.

The usual procedures for making apple sirup include neutralization of the acid with lime, calcium carbonate, or alkali carbonate (1, 2, 4, 5, 7, 10). This treatment, however, imparts undesirable flavors. Haines (6) added sugar to dilute the acid, which is common practice in preparing many fruit sirups. The apple sirup developed in this laboratory and used as a tobacco humectant (1, 7) is prepared by liming apple juice to a pH value of 8.0-8.5 to hydrolyze and precipitate the pectin, heating to 80° C., filtering, reacidifying to a pH value of 5.0-5.5 to improve color and flavor and prevent alkaline oxidation of sugars, and concentrating under vacuum to a total solids content of approximately 75%. The procedure described in this paper is similar, with the addition of ion-exchanger treatment before the liming step.

EXPERIMENTAL PROCEDURE

Before being passed through the exchanger beds, the juice was treated with activated carbon¹ and filtered with the aid of diatomaceous earth of medium porosity to remove colloidal material that might be absorbed by the exchanger with consequent reduction of its effective capacity. The clear filtrate was then treated

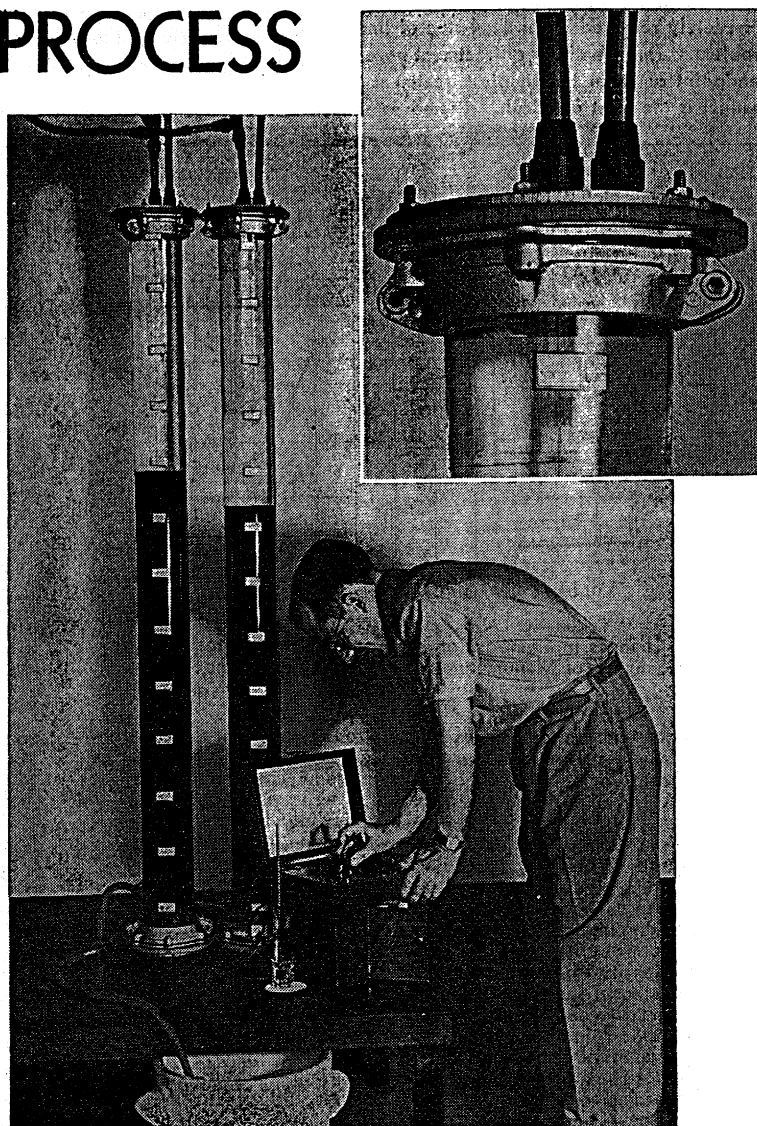


Figure 1. 4-Inch Exchanger Columns of Standard Pyrex Pipe and Flanges, with Saran Fittings; (Above) Means of Attaching Saran Fittings to Pyrex Pipe

with the ion-exchanger materials as described. After being treated, it was heated to 57° C. (135° F.) and limed until a flocculent precipitate appeared, usually at a pH value of 8.0 to 8.5. It was then filtered, reacidified with citric acid to a pH of 5.0 to 5.5, and evaporated under vacuum to 75% total solids.

Glass columns of 1-inch (25-mm.) and 4-inch (100-mm.) inside diameters were used for exchanger beds. The volumes of the beds were approximately 200 ml. and 7.5 liters, respectively. The 1-inch columns were set up in the conventional manner (9). The 4-inch columns (Figure 1) were constructed of standard 5-foot lengths of 4-inch Pyrex piping. The ends were closed by Saran flanges cut from a 3/8-inch sheet, backed by a 1/4-inch steel plate, and bolted to the piping with Corning companion flanges. The data reported here were obtained with the 1-inch laboratory columns, although similar results were obtained with the 4-inch columns.

¹ Later work has shown that carbon treatment is unnecessary and that passage of screened (150-mesh) but unfiltered juice through the exchangers reduces the capacity by only 10 to 15%. Before this procedure can be recommended, however, further work must be done to determine whether this reduction is cumulative or constant.

The removal of most of the malic acid from apple juice by anion adsorption avoids the bitter aftertaste of calcium malate formed by liming the original juice in the preparation of apple sirup. Anion adsorption also removes arsenic from spray residue. Lead is almost completely removed in the final step of liming and is not a serious problem. Three methods of treatment have been tested. From the standpoint of flavor the simplest treatment with a single anion exchanger is the most practical. It removes about 80 to 90% of the

acid and produces a palatable sirup with little flavor other than that of sweetness. A variable amount of arsenic is removed by the single treatment. To ensure more complete removal when it becomes necessary, a two-step (cation-anion) or a three-step (anion-cation-anion) exchanger treatment must be used. As much as 96% of the arsenic content has been removed by the three-step method, and a smaller amount has been eliminated by the two-step method. In addition, the cation exchanger removes about 90% of the ash.

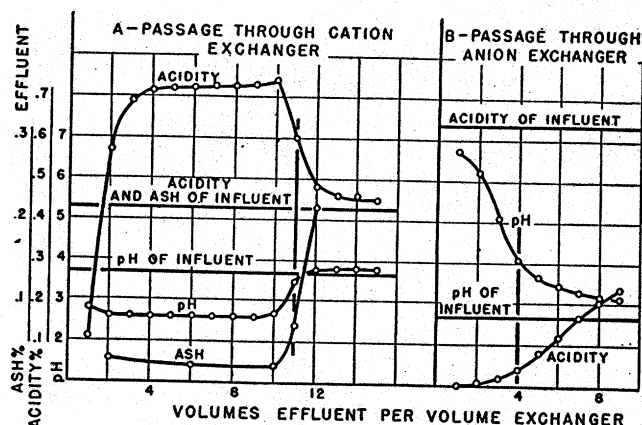


Figure 2. Changes in Composition of Apple Juice on Treatment with Exchangers (of Manufacturer A) According to Method II

The mode of action and general procedure for the use of ion exchangers has been discussed in detail elsewhere (8, 9, 12, 13). Juice was run downflow through the columns at a rate of 5 gallons (19 liters) per minute per square foot of cross-sectional area of the bed. After exhaustion, the beds were backwashed upflow with water at such a rate that there was a 50 to 75% expansion in the volume of the bed. After backwashing, the beds were regenerated. To regenerate the anion exchangers, four volumes of 4% sodium carbonate solution for each volume of exchanger were passed downflow at the rate of 2 gallons (7.6 liters) per minute per square foot of cross-sectional area. This quantity of regenerant was probably in excess of the amount actually needed but was used to ensure complete regeneration. To regenerate the cation beds, two volumes of 2%, or one volume of 4%, hydrochloric acid per volume of exchanger were found sufficient. The excess of regenerant was rinsed out downflow with water. The rinse water for the anion beds was softened by passage through a cation exchanger to avoid precipitation of insoluble carbonates by hard water. The progress of the reaction as the juice passed through the beds was followed by either the pH value or the titratable acidity of the effluent juice. With the cation exchangers, operating on a hydrogen cycle, there was a sharp change in pH and acidity at the break-through point; with the anion exchangers there was a gradual change, and the end point of the run had to be arbitrarily selected. The plotted data were obtained from successive samples taken during progress of the run.

In passage of juice through the cation-exchanger bed (Figure 2A) there was an increase in acidity and reduction in ash content as the bases were exchanged for hydrogen. The pH value decreased and remained at a constant level until the break-through point was reached, whereupon it increased rapidly to that of the influent juice. Thus, measurement of the pH value of the effluent served as an excellent means of determining the break-through point.

With the anion exchangers (Figure 3A) the pH value of the

first effluent was between 7.0 and 8.0; in succeeding fractions it gradually dropped until it approached that of the influent juice. Likewise, the acidity was at first zero but gradually increased and approached that of the influent, which indicated a gradual decrease in the efficiency of anion removal as the run progressed. Exhaustion of the exchanger was arbitrarily taken as the point at which the pH of the combined effluent was about 5.0. At this point there was about an 80% removal of acid from juice of average acidity. This end point is indicated by the vertical lines on the graphs.

CAPACITIES

DIFFERENT EXCHANGERS. "Capacity" is used to indicate the volume of effluent juice per volume of exchanger when the latter is considered exhausted. A more precise definition of capacity, in terms of equivalents of ions removed, is not practical in the case of apple juice because of its complex and varying nature:

Constituent	Per Cent	Constituent	Per Cent
Total sugar	9.6-12.0	Malic acid	0.11-1.68
Levulose	5.8-6.3	Other solids	0.48-2.35
Dextrose	0.5-3.5	Ash	0.22-0.41
Sucrose	0.6-3.9		

Figure 4 shows curves for pH vs. volume of effluent for cation exchangers of four manufacturers. The capacities of exchangers A and B were 13 volumes; those of C and D were 11 and 10 volumes, respectively. A, B, and C removed about 90% of the ash; D removed a slightly smaller amount, as Table I shows.

Table I. Ash Removed from Apple Juice by Cation Exchangers and Capacity of Exchangers

Exchanger	Ash ^a in Combined Effluent, %	Ash Removed, %	Capacity, Vol. Effluent per Vol. Exchanger
A	0.02	90.7	13
B	0.02	90.7	13
C	0.02	90.7	11
D	0.03	86.1	10

^a Ash of influent juice = 0.215%.

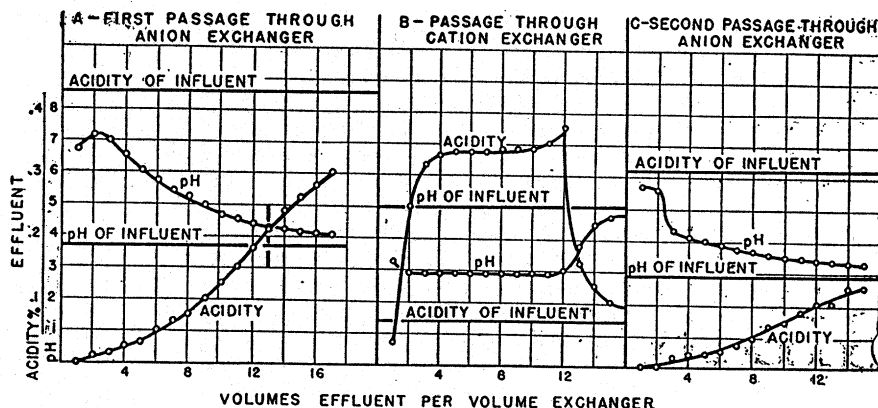


Figure 3. Changes in Composition of Apple Juice on Treatment with Exchangers (of Manufacturer A) According to Method III

Single treatment according to method I is illustrated by section on left.

The capacity of a cation exchanger naturally varied with the ash content of the juice. The tests just described were conducted on the same lot of juice; for different juices the capacities ranged from 10 to 40, the average being between 15 and 20.

The capacities of the different anion exchangers for the same juice varied over a wide range (Figure 4). The rapid drop in pH value shown by curves C and D indicates that the capacities of these two exchangers were low. Capacities of A and B were nearly equal and considerably higher than those of C and D.

JUICES OF DIFFERENT ACIDITY. Juices having a malic acid content ranging from 0.12 to 0.49% were used with anion exchanger A (Figure 5). The capacities ranged from 12 to 40 volumes and, in general, varied inversely with the acidity of the influent. However, the relation was not exact enough to use acidity as a means of predicting capacity. The reversal of order between juices V and VI might have been due to qualitative differences in the anions of the juices and their differential adsorption by the exchanger. The following generality may be permissible and useful: For apple juices of average acidity, 0.3 to 0.4%, the capacities of good anion exchangers range from 15 to 20.

METHODS FOR USING ION EXCHANGERS

Three methods of treating apple juice have been tested: (I) single treatment with an anion exchanger; (II) treatment with a cation exchanger followed by treatment with an anion exchanger; and (III) treatment first with an anion exchanger, then with a cation exchanger, and lastly with a second anion exchanger (suggested by F. I. L. Lawrence). Consideration was given to two other possible methods. One consisted in treating a limed juice by method II. This imposed a heavy load on the cation exchanger, owing to the added calcium, and was therefore abandoned. The other involved the use of a pectin-hydrolyzing enzyme before the anion exchanger treatment in method I, but this proved more expensive than the liming process and also produced darker sirup.

The simplest treatment is a single passage of the juice through an anion exchanger (method I). Figure 3A shows typical curves for pH and acidity of successive portions of the effluent juice; Figure 6 shows the percentage of acid removed from the combined effluent. From the thirteenth volume of the effluent, only about 50% of the acidity of the influent had been adsorbed, whereas from the combined 13 volumes about 82% of the acid had been removed. This represents an adsorption of about 47.5 grams of malic acid per liter, or 3 pounds per cubic foot of exchanger.

Since most of the free acid is removed by this treatment, only 0.020 to 0.025% lime is necessary to bring the pH value to 8.5 to hydrolyze the pectin, as compared with 0.25 to 0.30% required without anion-exchanger treatment. This liming process causes no increase in ash content; in fact a slight reduction may occur, probably because the added lime is precipitated as calcium pectate. Considerable color is occluded in the pectin precipitate. After the juice is filtered, only a small amount of citric acid is necessary to adjust the pH value to

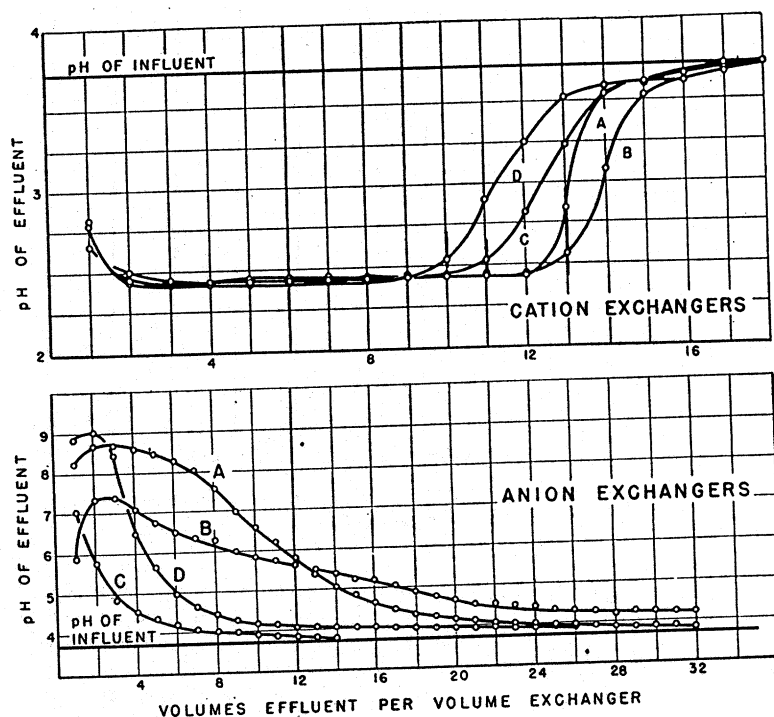


Figure 4. Effective Capacities of Cation and Anion Exchangers

between 5.0 and 5.5 before concentration. Removal of the malic acid prevents the formation of calcium malate and thus prevents the bitter aftertaste characteristic of sirups prepared without this treatment. The sirup contains the natural ash but has little flavor other than sweetness. Addition of the recovered volatile constituents of the juice produces a sirup with a pleasing apple flavor.

Although methods II and III effect a more complete removal of arsenic as compared with method I, flavor improvement is not sufficient to justify their use unless arsenic removal is necessary. Removal of arsenic is discussed in a later section.

In method II passage of the juice through the cation exchanger before passage through the anion exchanger converts combined acid to free acid and permits more complete adsorption of the anions. Figure 2 shows the ash, acidity, and pH values of the effluents from the cation and anion exchangers. The cation-exchanger treatment reduced the ash content by about 90% and increased the acidity from 0.43 to 0.64%. The increase in acidity reduced the volume of juice which could be treated by the anion exchanger in the next step, only four volumes passing through

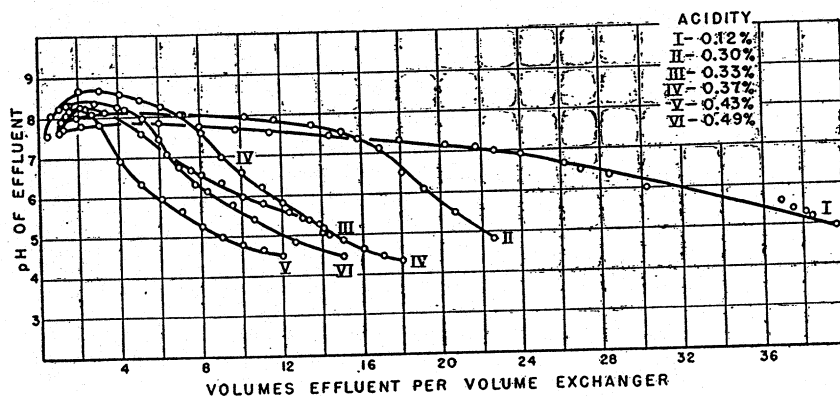


Figure 5. Effective Capacities of Anion Exchanger A with Juices of Different Acidity

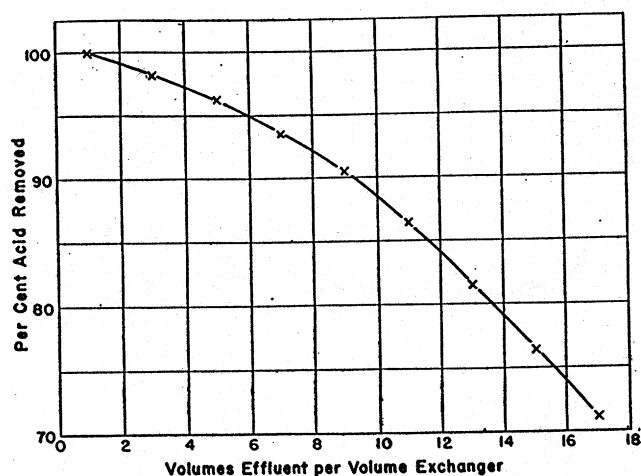


Figure 6. Removal of Acid from Juice as Measured in the Combined Effluent

before the pH value of the combined effluent reached 5.0, with an acidity of 0.02%. The more complete removal of buffer anions caused a lower acidity for the same pH value than that obtained by method I.

Figure 3 shows the pH and acidity values of the effluents obtained in method III, in which the juice was passed through anion, cation, and anion exchangers in succession. Comparison with Figure 2 shows that the capacity of the cation exchanger was increased by about two volumes by a previous anion-exchanger treatment. An increase in the juice capacity of the anion exchanger was also attained in this method, as compared with method II, by operating the first anion exchanger to a greater degree of saturation and using the second one as a scavenger to adsorb the acid that passed through the first. The acidity and pH value of the effluent from the second anion exchanger were so low that a pH value of 5.0 for the combined effluent was not practical for determining the exhaustion of the exchanger. The end point may be declared when the acidity of the combined effluent is 25% of that of the influent.

SPRAY RESIDUE REMOVAL

Since apple juice prepared from unwashed sprayed fruit may contain quantities of lead and arsenic which, in the prepared sirup, would be in excess of the tolerance, assuming a sixfold concentration of juice to sirup, it was considered advisable to determine the extent of lead and arsenic removal by ion exchanger treatment. Willits and Tressler (15) found that the base exchange material Zeo-Karb reduced the lead content of maple sap from as much as 36 p.p.m. to 1 p.p.m. or less. Lead is not so great a problem as arsenic, however, inasmuch as the liming process for precipitation of pectin removes almost all of the lead. In one instance liming without an anion exchanger treatment reduced the lead from 0.004 to 0.0002 grain per pound; in another case, after an anion exchanger treatment, liming reduced it from 0.005 to less than 0.0001 grain per pound. Passage through anion exchangers generally removed 20 to 50% of the lead, probably by precipitation as the hydroxide, since the pH increased as the fruit acids were removed. A cation exchanger removed only about 50% of the lead, possibly because of its presence in an un-ionized form.

Arsenic analyses were made on the juices (Table II) but were calculated to the basis of a sixfold concentration of juice to finished sirup, since the tolerance applies to the latter. Although most of the samples were low in arsenic, they exceeded the tolerance, especially sample 1, which was pressed from peels and cores. Since single passage of juice through an anion exchanger (method I) removed a small and variable amount of arsenic, this method would not be satisfactory for juice containing excessive amounts. However, adequate washing of the fruit before pressing might make this simple treatment satisfactory. To ensure a more complete removal of arsenic, other ion exchanger treatments could be used.

In method II passage of the juice through the cation exchanger prior to passage through the anion exchanger increased the adsorption of arsenic. Exchangers of manufacturer A removed 50 to 80% of the arsenic; exchangers of manufacturer B removed a smaller and more variable amount.

By the three-step treatment (method III), exchangers of manufacturer A were 96% effective, even in the high-arsenic sample (No. 1), and the final concentration was considerably below the tolerance. Smaller amounts were removed by the other exchangers.

The results show that arsenic can be successfully removed from apple juices by a suitable ion exchanger treatment. No data have been collected on the continued effectiveness of the anion exchangers in this respect. It is not known whether regeneration as ordinarily practiced completely removes the arsenic from the exchanger. Removal, however, might be effected by occasional regeneration with a concentrated solution of a strong acid, causing displacement of the more strongly adsorbed anion.

LIFE OF EXCHANGERS

An essential point in the use of ion exchangers is their effective life or capacity after many cycles. It is difficult to compare their capacities accurately when they are used with a natural product like apple juice because of its varied and varying composition. However, some of the laboratory columns have been used for seventy-five cycles with no noticeable loss in capacity.

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Table II. Arsenic Removed from Juice by Anion Exchangers in Terms of As_2O_3 per Pound of Sirup of 75% Solids

As ₂ O ₃ per Pound of Slurp or 10% solution									
Sample No.	Original, Grains per Lb.	Exchanger A		Exchanger B		Exchanger C		Exchanger D	
		Grains per lb.	% removed	Grains per lb.	% removed	Grains per lb.	% removed	Grains per lb.	% removed
Method I. Anion Exchanger									
1	0.156	0.114	26.9
2	0.0462	0.0456	1.3
3	0.033	0.0306	7.3
3	0.033	0.0234	29.2
3	0.033	0.0192	41.8
3	0.033	0.0186	43.6
4	0.027	0.0198	26.7
4	0.027	0.0252	6.7
4	0.027	0.0204	24.5
5	0.0228	0.0192	15.8
Method II. Cation-Anion Exchanger									
1	0.156	0.096	38.5
1	0.156	0.054	65.4
6	0.072	0.0636	11.7
6	0.072	0.012	83.4
3	0.033	0.0144	56.4
3	0.033	0.0108	67.3
4	0.027	0.0054	80.0
4	0.027	0.006	77.8
Method III. Anion-Cation-Anion Exchanger									
1	0.156	0.006	96.2
7	0.0618	0.0084	86.4	0.0162	73.8	0.0414	33.0	0.0156	74.6
8	0.0576	0.0048	91.7	0.0156	72.9	0.0276	52.1
3	0.033	0.0156	52.8
4	0.027	0.0006	97.8

Resinous Products & Chemical Company, which furnished the exchangers and gave helpful advice in carrying out the experiments. The contributions of Clara Day Rehrig and Nancy O'Connell Buck (formerly of this laboratory), who assisted in the analytical determinations and routine tests, are also acknowledged.

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